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Charge-density-wave superconductor $Bi_2Rh_3Se_2$

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We discovered a superconducting transition with the charge-density-wave state in a ternary compound $Bi_2Rh_3Se_2$. This compound crystallizes in the parkerite-type structure composed of sheets containing one-dimensional Rh-Rh chains. The electrical resistivity, magnetic susceptibility, thermoelectric power, sample length change, and x-ray diffraction measurements reveal that this compound is in the CDW state below 240 K. Furthermore, the specific heat and electrical resistivity measurements show a superconducting transition at ~0.7 K. The various superconducting parameters were determined, and the GL parameter $\kappa(0)$ shows the considerably large value of 151 indicating an extreme type-II superconductor.

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Collective states showing exotic electronic properties, such as superconductivity and charge-density-wave (CDW), have attracted a lot of interest. Peierls pointed out in his book that an electron-phonon interaction resulted in periodic and dielectric lattice distortions with a phase transition from metallic to insulating conductivity.[1] At the same time, Fröhlich suggested a sliding of the collective state involving lattice displacements and electrons in the one-dimensional metal as a mechanism of superconductivity.[2] His concept had been forgotten by an appearance of the Bardeen-Cooper-Schrieffer (BCS) theory but has revived in researches on the CDW state in one-dimensional conductors. The CDW state with such lattice distortions competes with a superconducting state because of the dielectric gapping of Fermi surface.

Recently, Gabovich and co-workers reviewed the properties of superconductors with CDW and discussed the competition between the CDW and superconducting states.[3,4] Most of the CDW superconductivities were found in compounds with the well-known crystal structures; i.e., layered chalcogenides, $NbSe_3$, *A*15-, and *C*15-type intermetallic compounds, and so on. In these compounds, partial dielectric gapping causes a detrimental effect on superconductivity.

In this study, we have synthesized successfully a novel ternary compound $Bi_2Rh_3Se_2$ and have investigated its crystal structure and transport properties. This compound is found to crystallize in a parkerite-type structure[5] composed of sheets containing one-dimensional Rh-Rh chains. As in metal-rich chalcogenides, a superconducting transition with the CDW state was first discovered through the electrical resistivity, magnetic susceptibility, specific heat, thermoelectric power, sample length change, and x-ray diffraction measurements.

A polycrystalline $Bi_2Rh_3Se_2$ was prepared by mixing Bi, Rh, and Se in the stoichiometric ratio and heating in a silica tube at 1320 K for 6 h. It was cooled slowly (2 K/h) to 1020 K, and then quenched. Unfortunately, we could not obtain products for a single crystal structure analysis because of formation of twin or much more crystals. Thus, the crystal structure of the obtained product was identified by powder x-ray diffraction measurements (Rigaku RINT 2000 diffractometer) between 30 and 300 K.

Magnetic susceptibilities were measured from 1.8 to 400 K in an applied field of 1 T using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5S). Electrical resistivity measurements were carried out in the temperature range of 0.35–400 K and in magnetic fields up to 1.5 T by a four-probe method in a Quantum Design PPMS equipped with a ^{3}He refrigerator. Specific heat measurement was performed from 0.35 to 300 K by the thermal relaxation method with the PPMS. The thermoelectric power (TEP) was measured in the temperature range between 10 and 300 K by a differential method. The sample length change was measured by using strain gauges from 5 to 300 K. The copper expansivities were used to convert the experimental relative length changes to the absolute values.

The x-ray diffraction measurement at room temperature reveals that the obtained product crystallizes in a parkerite-type structure as a single phase. By the Rietveld analysis using RIETAN2000,[6] the lattice parameters were determined to be $a=11.414(10)$ Å, $b=8.3709(9)$ Å, $c=11.989(1)$ Å, $\beta=89.153(3)°$ (reliable factors; $R_{wp}=12.9\%$, $R_I=4.2\%$).

The schematic crystal structure of $Bi_2Rh_3Se_2$ is illustrated in Fig. 1. In this structure, rhodium atoms are coordinated by selenium [d(Rh-Se)=2.39–2.41 Å], bismuth [d(Rh-Bi)=2.70–2.93 Å], and Rh [d(Rh-Rh)=2.86–2.99 Å]. The Rh-Rh bondings form one-dimensional chains along the *a*-axis having the short interatomic distances of d(Rh1-Rh4)=2.86 Å and d(Rh2-Rh3)=2.86 Å. These Rh chains are connected by Rh6 and Rh5 atoms with the longer Rh-Rh distances [d(Rh1-Rh6)=2.99 Å and d(Rh2-Rh5)=2.87 Å], forming two-dimensional sheets perpendicular to the *c* axis. The shortest interatomic distance between two-dimensional sheets is 3.25 Å for the Bi-Se bonding, and this feature of the pseudo-two-dimensional crystal structure will cause low-dimensional peculiar behavior.

Figure 2(a) shows the temperature dependence of the electrical resistivity ρ. A superconducting transition is observed at 0.9 K, as will be discussed later. Above 260 K, the resistivity increases linearly with temperature, indicating a

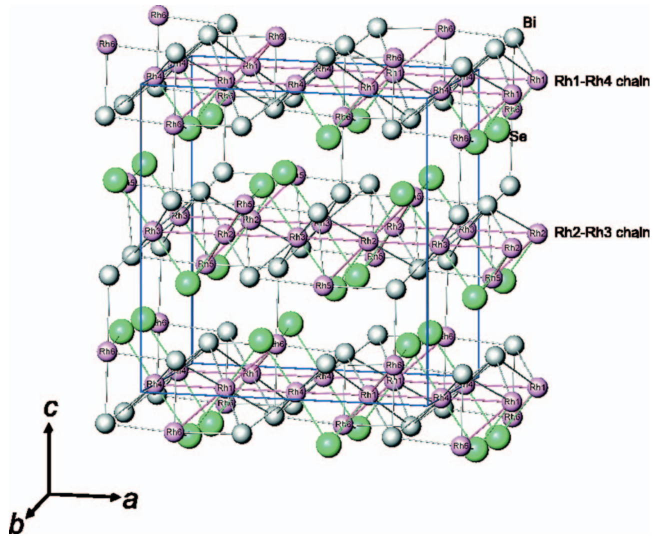

FIG. 1. (Color) Schematic crystal structure of $Bi_2Rh_3Se_2$.

typical metallic behavior. Below 250 K, the resistivity increases gradually with decreasing temperature and has a maximum around 190 K. Below 190 K, the resistivity shows a metallic behavior down to 1 K again. No hysteresis in the resistivity between the cooling and heating processes was observed around the anomaly temperature (~250 K), indicating that this phase transition is the second-order one.

Figure 2(b) shows the temperature dependence of the magnetic susceptibility χ after a diamagnetic correction ($\chi_{\text{dia}}=2.66\times10^{-4}$ emu mol^{-1}). The positive values of χ indicate that Pauli paramagnetism dominates the magnetic susceptibilities in this compound. A Curie paramagnetic behavior at low temperatures is attributable to a small amount ($<1.5\%$) of paramagnetic impurities which is undetectable in the x-ray diffraction profile. With decreasing temperature below 250 K, χ drops. The Pauli paramagnetic and Landau

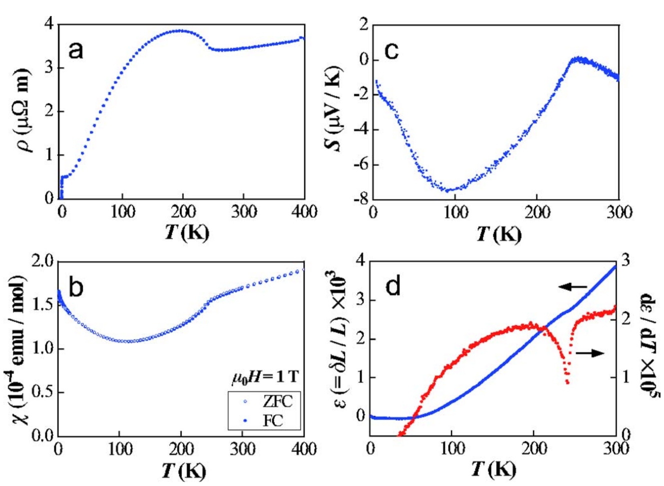

FIG. 2. (Color online) (a) Temperature dependence of the electrical resistivity (ρ). (b) Temperature dependence of the magnetic susceptibility (χ) in a magnetic field $\mu_0H=1$ T. (c) Temperature dependence of the thermoelectric power (S). (d) Temperature dependence of the sample length change (ϵ) and its first derivative ($d\epsilon/dT$).

diamagnetic susceptibilities can be represented by $\chi_{\text{Pauli}}+\chi_{\text{Landau}}=N_A\mu_0\mu_B^2[1-m^2/3m^{*2}]N(\epsilon_F)\propto N(\epsilon_F)$ using the density of states at the Fermi level $N(\epsilon_F)$. The drop of χ, which corresponds to the raise of ρ, indicates a loss of conduction electrons.

The temperature dependence of the thermoelectric power TEP for $Bi_2Rh_3Se_2$ is shown in Fig. 2(c). The TEP is negative over the whole temperature range. The value of TEP increases linearly with decreasing temperature and reaches a maximum at ~250 K. Below this temperature, TEP decreases rapidly, followed by a minimum at 95 K. Furthermore, with decreasing temperature, TEP increases toward zero and has a shoulder around 30 K ($\sim\Theta_D/6$; Θ_D is the Debye temperature) due to a phonon-drag, indicating a typical metallic behavior. The maximum at ~250 K is consistent with the onset of the anomaly as shown in the ρ-T and χ-T curves. Since the TEP measurement is a sensitive probe of the density of states close to the Fermi surface, the rapid change around 250 K is attributable to the sudden change of the band structure.

Figure 2(d) shows the temperature dependence of the sample length change $\epsilon(=\delta L/L)$. A shoulder is observed around 240 K in the ϵ-T curve. To clarify this anomaly, the first derivative of ϵ is also plotted in the same figure. A sharp peak is found at 242 K, indicating a lattice transformation in the $Bi_2Rh_3Se_2$. As observed in the T dependence of ρ, χ, TEP, and ϵ, it is considered that the second-order phase transition at ~250 K is caused by a deformation of the Fermi surface. Similar transitions are found in some CDW compounds.[3,4,7]

In order to clarify the anomaly at ~250 K due to the CDW transition, we have carried out the x-ray diffraction measurements below 300 K. Figure 3(a) shows the x-ray diffraction profiles at 100 and 300 K in which the logarithm value of intensity is plotted as the longitudinal axis. In the 2θ range between 10° and 40°, only one additional diffraction peak is found at ~35.5°. It is difficult to index this peak because of its broadness due to the overlap with some other reflections in this 2θ region. This superlattice peak at several temperatures is normalized [see Fig. 3(b)] and the integrated peak intensity is plotted as a function of temperature in Fig. 3(c). The superlattice reflection for a CDW phase gives directly the CDW gap Δ_{CDW}, i.e., the intensity is proportional to Δ_{CDW}^2.[7] According to the mean-field BCS theory, Δ_{CDW} can be represented by $\Delta_{\text{CDW}}(T)/\Delta_{\text{CDW}}(0)=\tanh\{(T_{\text{CDW}}/T)\times[\Delta_{\text{CDW}}(T)/\Delta_{\text{CDW}}(0)]\}$. The normalized Δ_{CDW}^2 is also plotted as a solid line in Fig. 3(c) and is in good agreement with the obtained superlattice intensities. This behavior is consistent with that for the CDW compounds $NbSe_3$, $(TaSe_4)_2I$ and $K_{0.3}MoO_3$. Unfortunately, we could not determine a wave vector of the CDW state from the powder x-ray diffraction. However, based on the results of the ρ, χ, TEP, ϵ, and low-temperature x-ray measurements, we can conclude that the anomaly at ~250 K is the second-order phase transition from the normal metallic state to the CDW state with metallic conductivity.

Figures 4(a) and 4(b) shows the temperature and field dependences of resistivity of $Bi_2Rh_3Se_2$, respectively. As shown in Fig. 4(a), the resistivity in the zero field drops

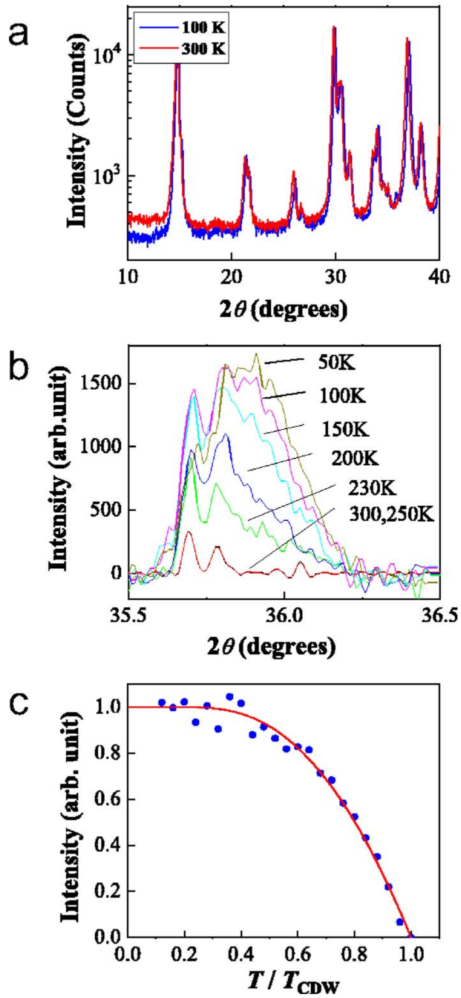

FIG. 3. (Color online) (a) Powder x-ray diffraction profiles at 100 and 300 K. (b) Powder x-ray diffraction profiles in the 2θ range between 35.5° and 36.5° at several temperatures. (c) Temperature dependence of the normalized superlattice integrated intensity.

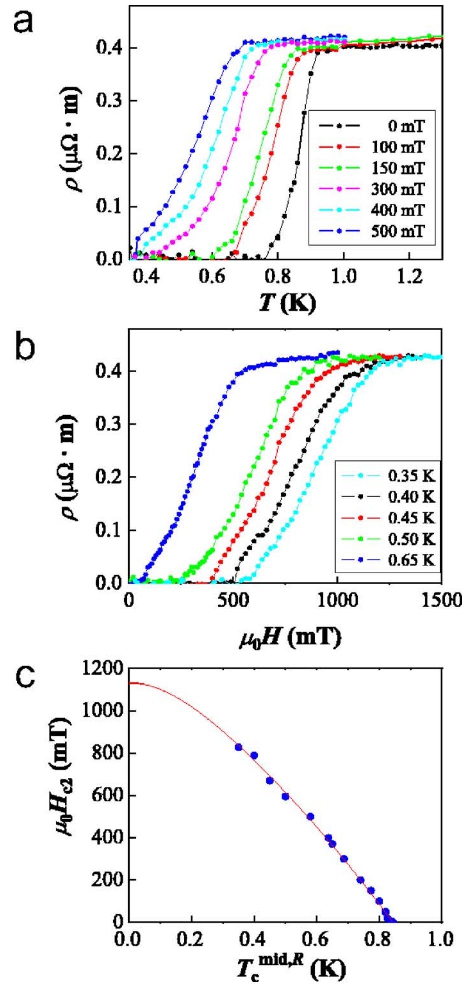

FIG. 4. (Color online) (a) Temperature dependence of the electrical resistivity (ρ) under various magnetic fields. (b) Field dependence of the electrical resistivity (ρ) at several temperatures. (c) Temperature dependence of the upper critical fields $[\mu_0 H_{c2}(T)]$ determined from the electrical resistivity data.

abruptly below 0.92 K with decreasing temperature, indicating a phase transition to a superconducting state. The zero resistivity is attained below 0.76 K. The critical temperature T_c is defined as the midpoint of the transition $T_c^{\mathrm{mid},R}$ $=0.84$ K.

The value of $T_c^{\mathrm{mid},R}$ decreases with increasing applied field [see Fig. 4(a)]. Assuming that $Bi_2Rh_3Se_2$ is a type-II superconductor, as will be justified below, the upper critical field $\mu_0 H_{c2}(T)$ was determined from Figs. 4(a) and 4(b). Figure 4(c) shows $\mu_0 H_{c2}(T)$ as a function of the critical temperature. According to the Werthamer-Helfand-Hohenberg (WHH) theory for a type-II superconductor in the dirty limit,[8] the upper critical field at zero temperature can be estimated from the relation $\mu_0 H_{c2}(0) = 0.693 T_c\,[-d\mu_0 H_{c2}(T)/dT] T \sim T_c$. The gradient $-d\mu_0 H_{c2}(T)/dT$ in the linear region near T_c is found to be about -1950 mT/K. Consequently, the $\mu_0 H_{c2}(0)$ value is found to be about 1130 mT. The Ginzburg-Landau (GL) coherence length at zero temperature $\xi_{\mathrm{GL}}(0)$ can be estimated to be 171 Å by the relation $\mu_0 H_{c2}(0) = \Phi_0 / 2\pi \xi_{\mathrm{GL}}(0)^2$.

The specific heat curves of C vs T below 300 K and C/T vs T^2 at low temperatures are given in Figs. 5(a) and 5(b), respectively. The C-T curve shows the anomalies at the temperatures of the CDW ($T_{\mathrm{CDW}} \sim 250$ K) and superconducting transitions ($T_c \sim 0.7$ K). A jump in the specific heat around 0.65 K is indicative of a bulk superconducting transition. The critical temperature from specific heat data is defined as the midpoint of the transition $T_c^{\mathrm{mid},C} = 0.66$ K. The specific heat in the normal state is composed of the electron and phonon contributions $C = C_e + C_{\mathrm{ph}}$. Above T_c and much below the Debye temperature Θ_D, C/T is expressed by $C(T)/T = (C_e + C_{\mathrm{ph}})/T = \gamma + 12R\pi^4 T^2 / 5\Theta_D^3$. From the C/T-T^2 plot in the normal metallic state, the values of γ and Θ_D were obtained to be 9.5 mJ/mol K^2 and 194 K, respectively. The electron-phonon coupling constant $\lambda_{e\text{-ph}}$ is estimated from the McMillan equation for the superconducting transition temperature $T_c = (\Theta_D / 1.45)\exp[-1.04(1+\lambda_{e\text{-ph}})/\lambda_{e\text{-ph}} - \mu^*(1+0.62\lambda_{e\text{-ph}})]$, where the Coulomb pseudopotential μ^* is assumed to be 0.13 empirically.[9] The value of $\lambda_{e\text{-ph}}$ is determined to be 0.45. This small $\lambda_{e\text{-ph}}$ value suggests that $Bi_2Rh_3Se_2$ is classified into a weak-coupling superconductor.

The electronic specific heat C_e was obtained by subtract-

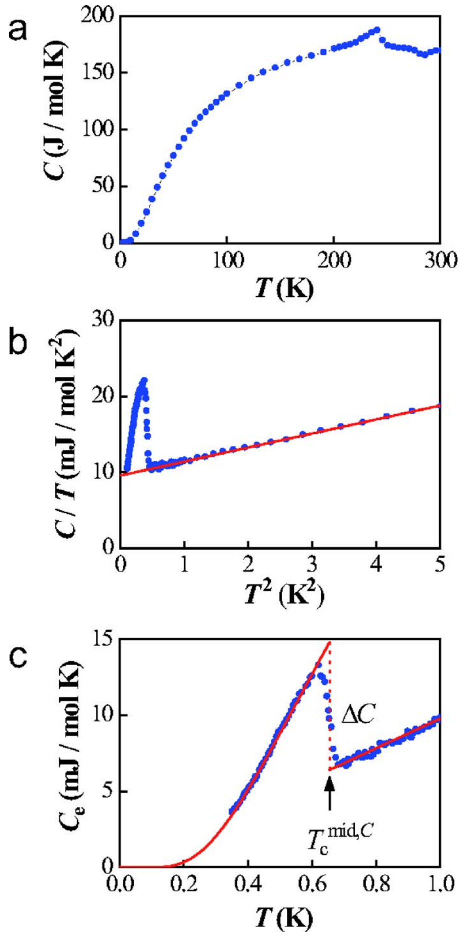

FIG. 5. (Color online) (a) Temperature dependence of the specific heat (C) below 300 K. (b) Temperature dependence of the specific heat divided by temperature (C/T) at low temperatures. (c) Temperature dependence of the electronic specific heat (C_e) below 1 K.

ing C_{ph} from the total C, and the temperature dependence of C_e is plotted in Fig. 5(c). The specific heat jump ΔC at $T_c^{\mathrm{mid},C}$ shows an evident energy gap in the superconducting state. Below T_c, the C-T data follows the exponential decay. On the other hand, the fitting of a T^n function gives poor results. These fitting result shows that $Bi_2Rh_3Se_2$ is an s-wave superconductor. The normalized specific heat jump value $\Delta C/\gamma T_c^{\mathrm{mid},C}$ is determined to be 1.35 and this value is slightly smaller than the limiting theoretical value ($\Delta C/\gamma T_c^{\mathrm{mid},C}=1.43$) of a weak-coupling superconductor. The result of the specific heat measurement reveals that $Bi_2Rh_3Se_2$ is a typical BCS weak-coupling superconductor.

The thermodynamic critical field $\mu_0 H_c(T)$ can be obtained as a function of temperature using the specific heat data in both normal the superconducting state. The difference in the entropy $\Delta S(T)$ between the normal and superconducting states was obtained from the thermodynamic relation $\Delta S(T)=S_n(T)-S_s(T)=\gamma T-\int_0^T[C_{es}(T')/T']dT'$, where $S_n(T)$ and $S_s(T)$ are the entropies in the normal and superconducting states, respectively, and C_{es} is the electronic specific heat in the superconducting state. The C_{es} below 0.35 K is extrapolated by the exponential curve. The value of $\mu_0 H_c(T)$ was obtained by the relation $G_n(T)-G_s(T)=\int_T^{T_c}[\Delta S(T')/T']dT'=\mu_0 V_m H_c(T)^2/2$, where V_m is the molar volume. The value of $\mu_0 H_c(0)$ is calculated to be 5.31 mT. On the other hand, the BCS theory predicts the magnitude of $\mu_0 H_c(T)$ by the relation $\mu_0 H_c(T)=[0.47\mu_0 \gamma T_c^2/V_m]^{1/2}$. The value of $\mu_0 H_c(0)$ is obtained to be 5.34 mT, which is close to the value of $\mu_0 H_c(T)=5.31$ mT obtained from the thermodynamic relation.

Moreover, the penetration depth $\lambda(0)$, GL parameter $\kappa(0)$ and lower critical field at zero temperature $\mu_0 H_{c1}(0)$, are estimated from the following relations: $\mu_0 H_c(0)=\Phi_0/2\sqrt{2}\pi\lambda(0)\xi_{\mathrm{GL}}(0)$, $\kappa(0)=\lambda(0)/\xi_{\mathrm{GL}}(0)$, $\mu_0 H_{c1}=\mu_0 H_c \ln \kappa/\sqrt{2}\kappa$. By using the value of $\mu_0 H_c(0)=5.31$ mT, $\lambda(0)$, and $\kappa(0)$, and $\mu_0 H_{c1}(0)$ are estimated to be 25700 Å and 151 and 0.12 mT, respectively. The considerably large value of $\kappa(0)$ indicates that $Bi_2Rh_3Se_2$ is an extreme type-II superconductor, like the high-T_c cuprates, fullerenes[10] and cobalt oxyhydrate.[11]

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